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Acetylene and Diacetylene

by

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REACTIONS OF $C_5H_3^+$ AND $C_5H_5^+$ IONS WITH ACETYLENE AND DIACETYLENE

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ABSTRACT

The reactions of $C_5H_3^+$ and $C_5H_5^+$ ions with acetylene and diacetylene were investigated using a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. The ejection capabilities of FTICR were used to determine the reaction mechanisms and rate constants for the reactions of ions produced from a number of precursors. While different structures could be attributed to $C_5H_3^+$ ions produced from different precursors on the basis of reactivity, this could not be done for $C_5H_5^+$ ions, whose reactivity was similar regardless of precursor. Different percentages of reactive $C_5H_5^+$ structure(s) were produced from various precursors using several charge transfer gases. Formation of $C_5H_5^+$ from norbornadiene and cycloheptatriene was studied in more detail and existence of a second formation mechanism was shown to be possible. Results are discussed in relation to previous work involving $C_3H_3^+$ and $C_5H_5^+$ reactions.

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and a proposed ionic route to soot formation.

INTRODUCTION

The $C_3H_3^+$ ion is found in quite high abundance in fuel-rich and sooting flames¹⁻³ and is postulated^{4,5} to react with neutrals such as acetylene, diacetylene, and C_2H in rapid, sequential condensation and condensation/elimination reactions, forming successively larger ions, which can rearrange to cyclic species during the ion/molecule reaction chain. According to the proposed^{4,5} ion/molecule mechanism of soot formation, $C_3H_3^+$ forms $C_5H_3^+$ and $C_5H_5^+$ in reactions with acetylene, and $C_7H_5^+$ when reacting with diacetylene. However, a previous study⁶ of the reactions of $C_3H_3^+$ with acetylene and diacetylene did not reveal facile formation of $C_5H_3^+$ or $C_5H_5^+$ by reaction of this ion with acetylene, although $C_3H_3^+$ did react readily with diacetylene, yielding $C_5H_3^+$ and $C_7H_3^+$. All three of the postulated products of $C_3H_3^+$ reactions with acetylene and diacetylene ($C_5H_3^+$, $C_5H_5^+$, $C_7H_5^+$) have been identified by mass spectrometry^{2,3} in flames, but it remains to be determined which, if any, of them may be important in soot formation mechanisms. Thus, as a continuation of earlier studies from these laboratories on ionic mechanisms of soot formation,⁶⁻¹¹ investigations have been extended to include study of the reactions of $C_5H_3^+$ and $C_5H_5^+$ ions with certain flame neutrals.

Heats of formation of the $C_5H_3^+$ ion from different precursors have been reported in three previous experimental studies.¹²⁻¹⁴ Dannacher, et al., suggested the presence of two different linear structures for $C_5H_3^+$, one produced by H loss from the 1,3-pentadiyne parent ion, and one by methyl loss from the 2,4-hexadiyne parent ion.¹⁴

There are many possible structures for the $C_5H_5^+$ ion, and despite a number of theoretical and experimental studies involving it, few definitive re-

sults exist regarding the specific relative energies of various isomeric forms.^{8,9} Experimental studies concentrated on determining the appearance potential and heats of formation of C₅H₅⁺ ions from different sources by mass spectrometric methods.^{12,15-20} These resulted in heat of formation values ranging from 239 to 309 kcal/mole depending on the source and technique of C₅H₅⁺ production.

Early ICR experiments in these laboratories were carried out to identify structures of C₅H₅⁺ according to their reactivity with different neutrals.⁸⁻¹⁰ Several precursors were used in the formation of C₅H₅⁺ ions and the results of the reactivity studies indicated the possibility of four different isomers of C₅H₅⁺.⁹ Acetylene reacted quite slowly with the C₅H₅⁺ ions,^{8,9} while diacetylene and aromatics with side chains reacted at an appreciable rate.⁸ As a result, it has been suggested that soot nucleation may proceed by adding a few large molecules rather than through addition of many smaller ones.^{8,11} No definitive assignment of C₅H₅⁺ isomeric structure was possible in the earlier studies.^{8,9} Proton-transfer reactions involving one relatively unreactive C₅H₅⁺ isomer gave⁸ a proton affinity of 227.9 ± 0.3 kcal/mol for the C₅H₄ neutral which remained after proton transfer. When combined with estimates of the heats of formation of possible C₅H₄ species, the results were consistent with (but did not conclusively prove) a vinyl cyclopropenyl form for the unreactive C₅H₅⁺ isomer.

A number of theoretical studies have examined C₅H₅⁺ structures.²¹⁻²⁶ Schleyer and co-workers located two minimum energy forms on the C₅H₅⁺ potential surface, the more stable one corresponding to planar cyclopentadienyl, the other one to a square-based pyramid structure.^{23,24} Similar results were reported by Stohrer and Hoffman²¹ although they proposed the pyramidal structure as the more stable form compared to the planar cyclopentadienyl.

Recent calculations by Zerner²⁷ have shown that the vinylcyclopropenylum isomer has the lowest energy ($\Delta H_f = 256.7$ kcal/mol) among a number of other possible structures such as the D_{5h} planar triplet and singlet, three open-chain species, methylenecyclobutylum, and the square-based pyramid. All of these structures were found to be no more than 30 kcal/mol higher in energy than the lowest energy structure.²⁷

In this work, the kinetics and reaction mechanisms of C₅H₃⁺ and C₅H₅⁺ ions produced from different precursors and reacting with acetylene and diacetylene have been studied in order to identify isomeric structures and to obtain rate coefficients. Also, the energetics of C₅H₅⁺ formation from norbornadiene and cycloheptatriene were followed to investigate two possible competing pathways of C₅H₅⁺ formation which could lead to different isomeric structures.

EXPERIMENTAL

Early ICR experiments were carried out on home-built ion cyclotron resonance mass spectrometers at the University of Florida and the National Bureau of Standards which have been described previously.^{8,9} A majority of the work reported here used a Nicolet FTMS-1000 Fourier transform ion cyclotron resonance (FTICR) mass spectrometer with a superconducting magnet of fixed magnetic field (3.0 tesla). Basic principles of the technique and its applications in ion/molecule reaction studies have been reviewed in several recent articles.²⁸⁻³⁰ Reaction pathways were delineated using the ejection capabilities³¹ of FTICR which make it possible to eject one ion from a complicated reaction mixture to determine its contribution to the mass spectrum of all the other ions.

Reaction rate coefficients were determined by monitoring the normalized

intensity of the $C_5H_3^+$ or $C_5H_5^+$ ions, respectively, as a function of time after ejection of all other ions from the analyzer cell. Details of rate coefficient determination are given in a previous paper.⁶ Excitation amplitude and total pressure were kept constant at optimized values for all the kinetic runs in order to minimize the unwanted effects of such factors on ion intensities, which have been discussed in detail elsewhere.³²

$C_5H_3^+$ ions were produced by 50 eV electron ionization of 2,4-hexadiyne and by reaction of $C_3H_3^+$ with diacetylene. The $C_3H_3^+$ ions used to produce $C_5H_3^+$ were formed by Xe^+ charge transfer reactions with propargyl iodide at an ionizing energy of 15 eV. After 30 ms reaction time with C_4H_2 , all the other ions except $C_5H_3^+$ were ejected from the cell to follow the reactions of this ion with diacetylene as a function of time. The $C_5H_5^+$ ions were produced by charge transfer reactions of dicyclopentadiene, cyclopentadiene, norbornadiene, 1-penten-3-yne, and cycloheptatriene with different charge transfer agents (Xe^+ , N_2^+ , Ar^+) formed with an electron beam pulse of 5 ms duration at an ionizing energy of 13, 16.5, and 20 eV, respectively.

Cyclopentadiene was prepared by cracking dicyclopentadiene³³ and was kept in dry ice when not used to prevent the dimerization process. Diacetylene was prepared by dehydrochlorination of 1,4-dichloro-3-butyne in aqueous potassium hydroxide/dioxane solution.³⁴ All the other compounds used were obtained commercially and their purity was checked by obtaining wide mass range spectra. All the samples were used after multiple freeze-pump-thaw cycles.

All reactions were followed at a cell temperature of 363 K. Some $C_5H_3^+$ and all $C_5H_5^+$ ions used in rate constant determination studies were produced by ion/molecule reactions in order to minimize the internal energy imparted to the ions. Also, since the total pressure in the reaction cell was almost 1×10^{-5} torr and the reactant ion formation time was >30 ms, substantial col-

lisional relaxation of the ions took place before kinetic data were collected.

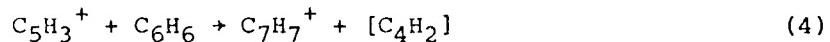
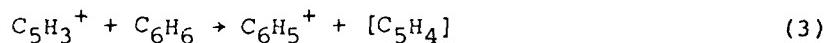
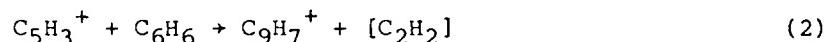
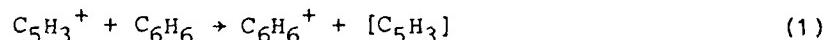
All neutral pressures reported in this work were measured using an ionization gauge and then corrected by comparison to a capacitance manometer.

RESULTS

Reactions of C₅H₃⁺

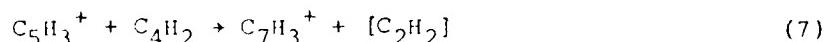
A very low number of C₅H₃⁺ ions were produced from 2,4-hexadiyne at electron energies above 30 eV. Reactivity of these ions was monitored at an electron energy of 50 eV although the ion intensity was still very low. Although almost all of the C₅H₃⁺ ions produced reacted with the 2,4-hexadiyne precursor, no reaction was observed with either C₂H₂ or C₄H₂.

Reactions of C₅H₃⁺ with 2,4-hexadiyne were:



C₅H₃⁺ ions produced as products of the reaction of C₃H₃⁺ with C₄H₂ were 100% reactive with both propargyl iodide and diacetylene (the neutrals present in the reaction medium).

C₅H₃⁺ reactions with C₄H₂ were:

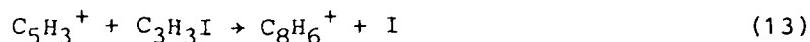




Some of the product ions were observed to react further with propargyl iodide by displacing atomic iodine:



C_5H_3^+ reactions with propargyl iodide were:



The C_8H_6^+ ion reacted further with C_4H_2 :



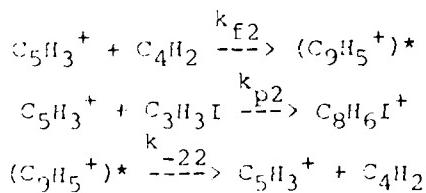
Ion intensity vs. time curves for the $\text{C}_5\text{H}_3^+ / (\text{C}_4\text{H}_2 + \text{C}_3\text{H}_3\text{I})$ system are shown in Figure 1. The decay of C_5H_3^+ ions involved reaction with both C_4H_2 and propargyl iodide.

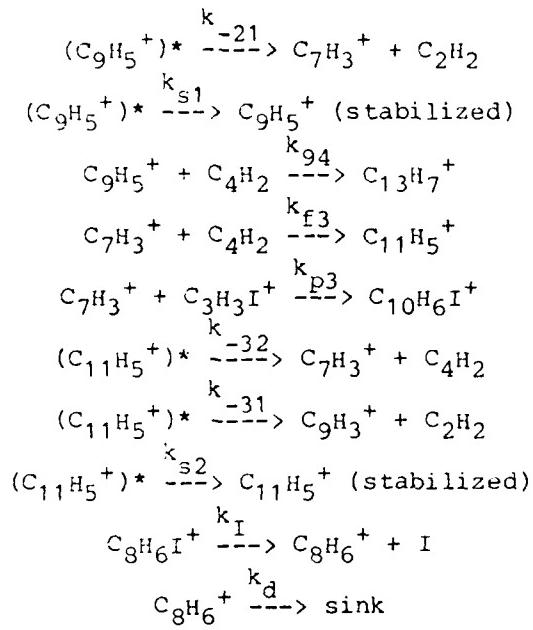
The procedure for rate coefficient determination used in previous studies of C_3H_3^+ and C_5H_3^+ ion/molecule reactions^{6,9,11} required subtraction of the observed rate constant for the reaction of the ion with the precursor neutral from the observed rate constant for the sum of the reactions with precursor and reactant neutrals. In this case, however, the reactant neutral (C_4H_2) was also the precursor of the ion of interest (C_5H_3^+), and thus the subtraction procedure could not be used. An alternative method for rate constant determination was thus required. Following ejection of all other ions from the FTICR cell, the decay of C_5H_3^+ as a function of time is given by $[\text{C}_5\text{H}_3^+]$

$= [C_5H_3^+]_0 e^{-(n_p k_p + n_d k_d)t}$, where $n_p k_p$ and $n_d k_d$ refer to the products of the number densities and ion/molecule rate coefficients for propargyl iodide and diacetylene, respectively (Reactions (7), (8), and (13)). The quantity $n_d k_d + n_p k_p$ can thus be determined from the slope of a semilog plot of $C_5H_3^+$ decay as a function of time. At short reaction times, the following expressions hold true: $dD/dt = n_d k_d [C_5H_3^+]_0 e^{-(n_p k_p + n_d k_d)t}$ and $dP/dt = n_p k_p [C_5H_3^+]_0 e^{-(n_p k_p + n_d k_d)t}$ where D and P refer to product ions of the reaction with diacetylene ($C_7H_5^+$ and $C_9H_5^+$, (Reactions (7) and (8)) and with propargyl iodide ($C_8H_6^+$, Reactions (13)), respectively. Thus, the ratio $n_d k_d/n_p k_p$ was calculated from the ratio of slopes of product formation as a function of time. Next $n_d k_d$ was obtained using the calculated sum and ratio of the two rate constants. Finally the absolute rate constant was determined following the usual procedure.⁶ It was found that $C_5H_3^+$ ions reacted with C_4H_2 with a rate constant of $(5.6 \pm 1.7) \times 10^{-10} \text{ cm}^3/\text{s}$.

Kinetic Modeling of $C_5H_3^+$ reactions with diacetylene

In order to better understand the reaction mechanisms involved in the $C_5H_3^+ + C_4H_2$ reaction system, kinetic modeling studies of the ion intensity vs. time curves shown in Fig. 1 were carried out. Details of the modeling methodology are given elsewhere.³⁵ A kinetic model involving the reactions above was fitted to the experimental data assuming steady-state concentrations for the excited forms of $(C_7H_5^+)^*$, $(C_8H_6^+)^*$, $(C_9H_5^+)^*$ and $(C_{11}H_5^+)^*$ intermediate complexes. The following reaction scheme shows all steps used.





(Scheme A)

Comparison of the model fit with the experimental data is shown in Figures 2a and 2b. The actual fitting parameters and best fit values obtained were

$$\theta_2 = -8.7(.2)\text{s}^{-1}$$

$$\theta_3 = -4.6(.4)\text{s}^{-1}$$

$$k_{-21}\phi_1 = 2.8(.1)\text{s}^{-1}$$

$$k_{s1}\phi_1 = 3.7(.1)\text{s}^{-1}$$

$$k_{s2}\phi_2 = 2.9(.2)\text{s}^{-1}$$

$$k_{34} = .04(.06)\text{s}^{-1}$$

$$k_d = .8(.2)\text{s}^{-1}$$

where $\theta_2 = -(k_{-21} + k_{s1})k_{f2}P_{\text{C}_4\text{H}_2}/(k_{-21} + k_{-22} + k_{s1}) - k_{p2}P_{\text{C}_3\text{H}_3\text{I}}$, $\theta_3 = -(k_{-31} + k_{-32})k_{f3}P_{\text{C}_4\text{H}_2}/(k_{-31} + k_{-32} + k_{s2}) - k_{p3}P_{\text{C}_3\text{H}_3\text{I}}$, $\phi_1 = k_{f2}P_{\text{C}_4\text{H}_2}/(k_{-21} + k_{-22} + k_{s1})$ and $\phi_2 = k_{f3}P_{\text{C}_4\text{H}_2}/(k_{-31} + k_{-32} + k_{s2})$.

$C_5H_5^+$

Effect of Precursor Neutrals: $C_5H_5^+$ ions produced from different precursors exhibited behavior indicative of both reactive and unreactive populations toward both the precursors and the reactant neutrals. Figures 3a and 3b show $C_5H_5^+$ normalized ion intensity vs. time curves for two (1,3,5-cycloheptatriene and 1-penten-3-yne) of the five precursors used to form ions before reaction with diacetylene and acetylene. Following an exponential decay indicative of pseudo-first order kinetics, a substantial fraction of unreactive ions remains at long reaction times, particularly in Figure 3b. Table I shows the method of preparation of $C_5H_5^+$ ions from different precursors and the percent of unreactive ions remaining at long reaction times.

Two (norbornadiene and cycloheptatriene) of the five precursors mentioned above produce $C_7H_8^+$ rather than $C_5H_6^+$ parent ions. The $C_7H_8^+$ ions produced from norbornadiene were reported^{36,37} earlier to lead to two different channels (Reactions (16) and (17)), for $C_5H_5^+$ ion formation.



or



Thus, $C_5H_5^+$ ion formation pathways have been studied in more detail for norbornadiene and cycloheptatriene. When different charge transfer gases were used for ionization of norbornadiene, different percentages of reactive $C_5H_5^+$

were observed, as is noted in Table I. Also the abundances of $C_7H_7^+$, $C_5H_6^+$ and $C_5H_5^+$ ions were measured following charge transfer ionization, and different behavior was observed for compounds with ionization potentials in the range of 14 to 16 eV. Table II shows this effect for two reagent gases (Fr^+ and N_2^+) which have ionization energies of 14.0 and 15.7 eV respectively.

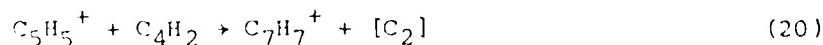
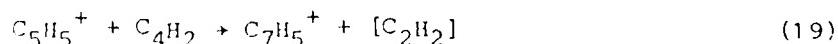
In order to further investigate this behavior, the relative ion abundances vs. electron energy for cycloheptatriene and norbornadiene were obtained (see Figures 4 and 5). Electron impact ionization was used for this study and therefore the energy scale in Figures 4 and 5 should be considered as approximate with at least ± 1 eV uncertainty.

$C_5H_5^+$ reactions with diacetylene

After ejection of all ions except $C_5H_5^+$ following charge transfer chemical ionization of a mixture of diacetylene and a precursor compound, the ion/molecule reactions as a function of time were monitored. Independent of the precursor used, the main reaction was the addition of C_4H_2 to $C_5H_5^+$ to produce the $C_9H_7^+$ ion.



Other minor reactions observed were:



For $C_5H_5^+$ ions produced from cyclopentadiene, the C_2 addition reaction (19) was not observed with C_4H_2 .

The rate coefficient for the disappearance of $C_5H_5^+$ was calculated as described earlier⁶ and the values found for $C_5H_5^+$ ions produced from different precursors are given in Table III.

$C_5H_5^+$ reactions with acetylene

$C_5H_5^+$ ions formed from four of the five precursors (cyclopentadiene, 1-penten-3-yne, norbornadiene, cycloheptatriene) reacted very slowly with C_2H_2 , producing very small amounts of $C_7H_7^+$ and $C_9H_9^+$.



Rate constants for the $C_5H_5^+ + C_2H_2$ reaction were about one order of magnitude less than those for reactions with C_4H_2 (see Table III).

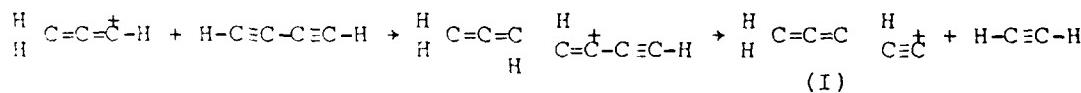
DISCUSSION

$C_5H_3^+$

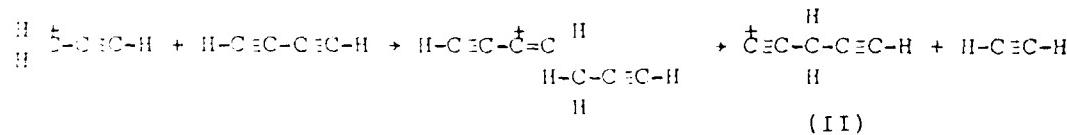
Two different $C_5H_3^+$ structures were postulated following PIPECO measurements of the appearance energy of $C_5H_3^+$ ions from 1,3-pentadiyne and 2,4-hexadiyne. In the work reported here, $C_5H_3^+$ ions were produced from 2,4-hexadiyne and from reaction of $C_3H_3^+$ with diacetylene. Although $C_5H_3^+$ ions produced either way were reactive toward their precursor neutrals, $C_5H_3^+$ ions from 2,4-hexadiyne were unreactive with both C_4H_2 and C_2H_2 , while those formed as ion/molecule reaction products reacted with C_4H_2 with the relatively high rate constant of $(5.6 \pm 1.7) \times 10^{-10} \text{ cm}^3/\text{s}$. Dannacher et al.¹⁴ suggested the

structures $\text{CH}_3-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}^+$ and $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CH}_2^+$ for the C_5H_3^+ ions produced from 2,4-hexadiyne and 1,3-pentadiyne respectively. Experimental values of the heat of formation of these ions suggested that the former probably had a higher heat of formation (<1431 kJ/mole)¹³ compared to the latter (1317 kJ/mole).¹⁴ In this study, higher reactivity of C_5H_3^+ ions produced by the $\text{C}_3\text{H}_3^+ + \text{C}_4\text{H}_2$ reaction compared to those produced by electron ionization of 2,4-hexadiyne suggests that the former have a higher heat of formation with a stable structure different from those reported earlier for C_5H_3^+ ions from both 2,4-hexadiyne and 1,3-pentadiyne. Enhanced reactivity does not always correlate with a higher heat of formation, but this has often been found true for isomers of other small hydrocarbon ions. Our observation that C_5H_3^+ is formed in an exothermic reaction of linear C_3H_3^+ with diacetylene leads to an upper limit of 1375.9 kJ/mol for ΔH_f of the C_5H_3^+ ion formed in this manner.³⁸ This value is not inconsistent with either of those reported earlier.

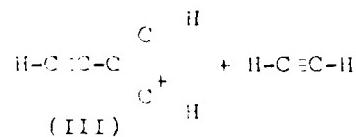
Reaction of the propargylium cation with diacetylene, with resultant loss of acetylene, might proceed according to either Scheme B or Scheme C.



Scheme B



or/and



Scheme C

The three possible $C_5H_3^+$ product ions in the above schemes have structures which differ from those postulated¹⁴ earlier. While no definitive theoretical or experimental evidence as to the relative stability of these (or other) $C_5H_3^+$ isomers is available, (III) is most similar to the vinylcyclopropenylum ion found²⁷ most stable among the $C_5H_5^+$ isomers. Thus (I) or (II) might be the unstable, reactive structure formed in these experiments.

Preliminary INDO calculations⁴² show that III is considerably more stable than the geometry-optimized form of II (by 74 kcal/mol) which in turn is more stable (160 kcal/mol) than the geometry-optimized form of III. Of course, cyclic structures such as III are favored in INDO calculations, so more detailed calculations will be necessary to assess the relative stabilities of the three isomers.

$C_5H_5^+$ ion structures produced from different precursors

$C_5H_5^+$ ions produced from different precursors all exhibited at least two populations, one reactive, other unreactive. This behavior for numerous other ionic reactants has been used previously⁴³⁻⁴⁶ to argue for the existence of at least two different structural isomers; one reactive and one non-reactive. These results are in agreement with the earlier reactivity study of $C_5H_5^+$ ions from different precursors.⁹ To distinguish the reactive $C_5H_5^+$ structures, their reaction mechanisms and reaction rates with acetylene and diacetylene were studied. Although they reacted with their precursor neutrals with different rates, they all reacted with acetylene and diacetylene at similar rates within the experimental error limits, as shown in Table III. Thus no isomeric differentiation based on reactivity can be made. Rate coefficients for the reaction with acetylene were similar to those determined earlier,^{8,9} i.e. in the range of 10^{-11} cm³/s. Reaction mechanisms were similar for all

$C_5H_5^+$ ions with the exception of cyclopentadiene, which did not give C_2 addition reactions with C_4H_2 . More definitive identification of $C_5H_5^+$ structures may be forthcoming when better theoretical calculations²⁷ have been reported, although identification of the vinylcyclopropenylum ion as (one of) the unreactive structure(s) seems reasonable in light of the calculations²⁷ and earlier ICR studies.⁸

To compare the behavior of ions produced from 1,3,5-cycloheptatriene and norbornadiene precursors (both having the formula C_7H_8), relative abundances as a function of electron energy shown in Figures 4 and 5 were obtained. As shown, the curves for $C_7H_7^+$ (Figures 4a and 5a) and $C_5H_5^+$ and $C_3H_3^+$ (Figures 4b and 5b) are very similar both in terms of energetics and of general shape. Differences in $C_5H_5^+$ relative intensities are probably due to the normalization procedure used in each case. An increase in the relative intensity of $C_5H_5^+$ ions in both cases in the energy range of 15-25 eV along with the fact that the $C_7H_7^+$ curves no longer increase in this energy range implies that most of the $C_5H_5^+$ ions are produced from $C_7H_7^+$. Similar behavior is seen for $C_3H_3^+$ ions, i.e., the intensity of these ions increases at about 22 eV (on the energy scale shown on Figure 4b and 5b) where the rate of increase in intensity of $C_5H_5^+$ is decreased. This similar behavior implies that $C_7H_7^+$ ions formed from 1,3,5-cycloheptatriene and norbornadiene follow the same fragmentation pathways in the same energy range. Similar behavior for $C_7H_7^+$ ions from these two compounds has also been reported earlier in collisional activation studies.⁴⁷

As seen in Figures 4b and 5b formation of $C_5H_6^+$, both in terms of energetics and relative intensity, is different for cycloheptatriene and norbornadiene, indicating that $C_7H_8^+$ ions formed from these compounds by electron impact have different structures (according to Reaction 17a). Based

on the significantly higher relative intensity of $C_5H_6^+$ for norbornadiene along with the results shown in Tables I and II, there exists the possibility of formation of $C_5H_5^+$ ions from the $C_5H_6^+$ channel by Reaction 17b for norbornadiene. As shown in Table I, for norbornadiene the percent of unreactive $C_5H_5^+$ increases from 5-10% to 18-20%. When the ionizing charge transfer energy increases from 14.0 eV to 15.7 eV, while no such change in $C_5H_5^+$ reactivity was observed for cycloheptatriene under the same conditions. Relative ion intensities at two different energies for charge transfer chemical ionization are shown in Table II for norbornadiene. The results indicate that when Ar^+/N_2^+ replaces Kr^+ as a charge donor, the relative intensity of the observed $C_5H_5^+$ increases while there is a corresponding decrease in the yield of the $C_5H_6^+$ ion. Thus, evaluation of the results on $C_5H_5^+$ reactivity (Table I) together with the results on the relative ion intensity (Table II) implies that $C_5H_5^+$ formed from the $C_5H_6^+$ channel has a higher percent of unreactive isomer compared to that formed from the $C_7H_7^+$ channel. Similar results were also reported earlier for norbornadiene.^{36,37}

In general, a similar trend in ion/molecule reactivity with acetylene and diacetylene has been found for $C_5H_5^+$ ions as was seen⁶ for $C_3H_3^+$ ions: little or no reactivity with acetylene, but extensive and rapid reactivity with diacetylene. The results of bimolecular reactivity studies on both $C_3H_3^+$ and $C_5H_5^+$ suggest that the proposed ion/molecule condensation reactions with diacetylene in the ionic soot formation mechanism are quite credible while the proposed sequential acetylene addition reactions should be reconsidered. These experiments and those reported earlier⁶ were carried out at relatively low pressures ($p < 5 \times 10^{-5}$ torr). It is thus quite possible that third-body collisions in atmospheric pressure flames can stabilize a larger fraction of

the $C_7H_7^+$ reaction complexes and result in increased reactivity with acetylene. In fact, such collisional stabilization of the association complexes for the reactions of $C_3H_3^+$ and $C_4H_4^+$ with C_2H_2 has been shown to occur in higher pressure SIFT studies,^{48,49} although no such stabilization was observed under ICR experimental conditions.^{50,51}

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Table I: Percentages^a of unreactive $C_5H_5^+$ found from various precursors by charge transfer chemical ionization monitored by observing reaction with the precursor neutral.

Precursor neutral	Ionizing technique	Percent unreactive $C_5H_5^+$
dicyclopentadiene	N_2^+/Ar^+ charge transfer	20
cyclopentadiene	Xe^+ charge transfer	17
1-penten-3-yne	Xe^+ charge transfer	65-70
cycloheptatriene	Ar^+ charge transfer	0-5
norbornadiene	N_2^+/Ar^+ charge transfer	18-20
	Kr^+ charge transfer	5-10

^a Estimated error is $\pm 5\%$.

Table II: Changes in ion abundances at two different ionization energies for norbornadiene.

Ionizing energy/eV (ionizing technique)	Abundances as a fraction of total ion signal ^a			
	$C_7H_8^+$	$C_7H_7^+$	$C_5H_6^+$	$C_5H_5^+$
14.0 (Kr^+ charge transfer)	0.07	0.45	0.32	0.16
15.7 (N_2^+ charge transfer)	0.09	0.28	0.16	0.47

^a Estimated error is ± 0.03 .

Table III: Rate coefficients for the reaction of $C_5H_5^+$ ions from different precursors^a with diacetylene and acetylene.

Precursor	Diacetylene	Acetylene
	Absolute rate coefficient/ $(10^{-10} \text{ cm}^3/\text{s})$	Absolute rate coefficient/ $(10^{-11} \text{ cm}^3/\text{s})$
cyclopentadiene	1.0 ± 0.5	4.8 ± 1.9
1-penten-3-yne	2.0 ± 1.0	2.7 ± 1.0
norbornadiene	2.9 ± 1.4	3.1 ± 1.3
cycloheptatriene	3.3 ± 1.9	1.8 ± 0.7
dicyclopentadiene	1.6 ± 0.8	b

^a $C_5H_5^+$ ions were produced by charge transfer chemical ionization using different gases as shown in Table I.

^b Ion signal for dicyclopentadiene was too small to produce reproducible results for the rate coefficient.

FIGURE CAPTIONS

Figure 1. Reactions of $C_5H_3^+$ with C_4H_2 . $C_5H_3^+$ (□), $C_7H_3^+$ (+), $C_9H_5^+$ (◇) and $C_{11}H_5^+$ (Δ). Disappearance of $C_5H_3^+$ and product ions includes reactions with propargyl iodide. $C_5H_3^+$ ions were produced from the reaction of $C_3H_3^+$ with diacetylene within 30 ms reaction time. $C_3H_3^+$ ions were produced from propargyl iodide by charge transfer reactions with Xe. $P_{C_3H_3I} = 1.9 \times 10^{-7}$ torr, $P_{C_4H_2} = 1.3 \times 10^{-6}$ torr, $P_{Xe} = 5.4 \times 10^{-6}$ torr.

Figure 2a and 2b. Model fit to a typical data set for $C_5H_3^+ + C_4H_2$ reactions including both the decay curve for $C_5H_3^+$ and the formation curves for various product ions as a function of time.

Figure 3a. $C_5H_5^+$ ion decay curves for reactions with cycloheptatriene(◇), cycloheptatriene and acetylene, and cycloheptatriene and diacetylene(□). $C_5H_5^+$ ions were produced from cycloheptatriene by charge transfer reactions with Ar⁺. $P_{C_7H_8} = 1.3 \times 10^{-7}$ torr, $P_{C_2H_2} = 1.1 \times 10^{-6}$ torr, $P_{C_4H_2} = 6.6 \times 10^{-7}$ torr, $P_{Ar} = 10.4 \times 10^{-6}$ torr.

Figure 3b. $C_5H_5^+$ ion decay curves for reactions with 1-penten-3-yne(□), 1-penten-3-yne and acetylene(+), and 1-penten-3-yne and diacetylene(◇). $C_5H_5^+$ ions were produced from 1-penten-3-yne by charge transfer reactions with Ar⁺. $P_{C_5H_6} = 4.2 \times 10^{-7}$ torr, $P_{C_2H_2} = 1.4 \times 10^{-6}$ torr, $P_{C_4H_2} = 8.4 \times 10^{-7}$ torr, $P_{Ar} = 5.4 \times 10^{-6}$ torr.

Figure 4a. Relative intensities of $C_7H_8^+$ (+) and $C_7H_7^+$ (□) ions produced from cycloheptatriene as a function of electron impact energy.

Figure 4b. Relative intensities of $C_5H_6^+(\diamond)$, $C_5H_5^+(+)$, and $C_3H_3^+(\square)$ ions produced from cycloheptatriene as a function of electron impact energy.

Figure 5a. Relative intensities of $C_7H_8^+(+)$ and $C_7H_7^+(\square)$ ions produced from norbornadiene as a function of electron impact energy.

Figure 5b. Relative intensities of $C_5H_6^+(\diamond)$, $C_5H_5^+(+)$, and $C_3H_3^+(\square)$ ions produced from norbornadiene as a function of electron impact energy.

FIGURE 1

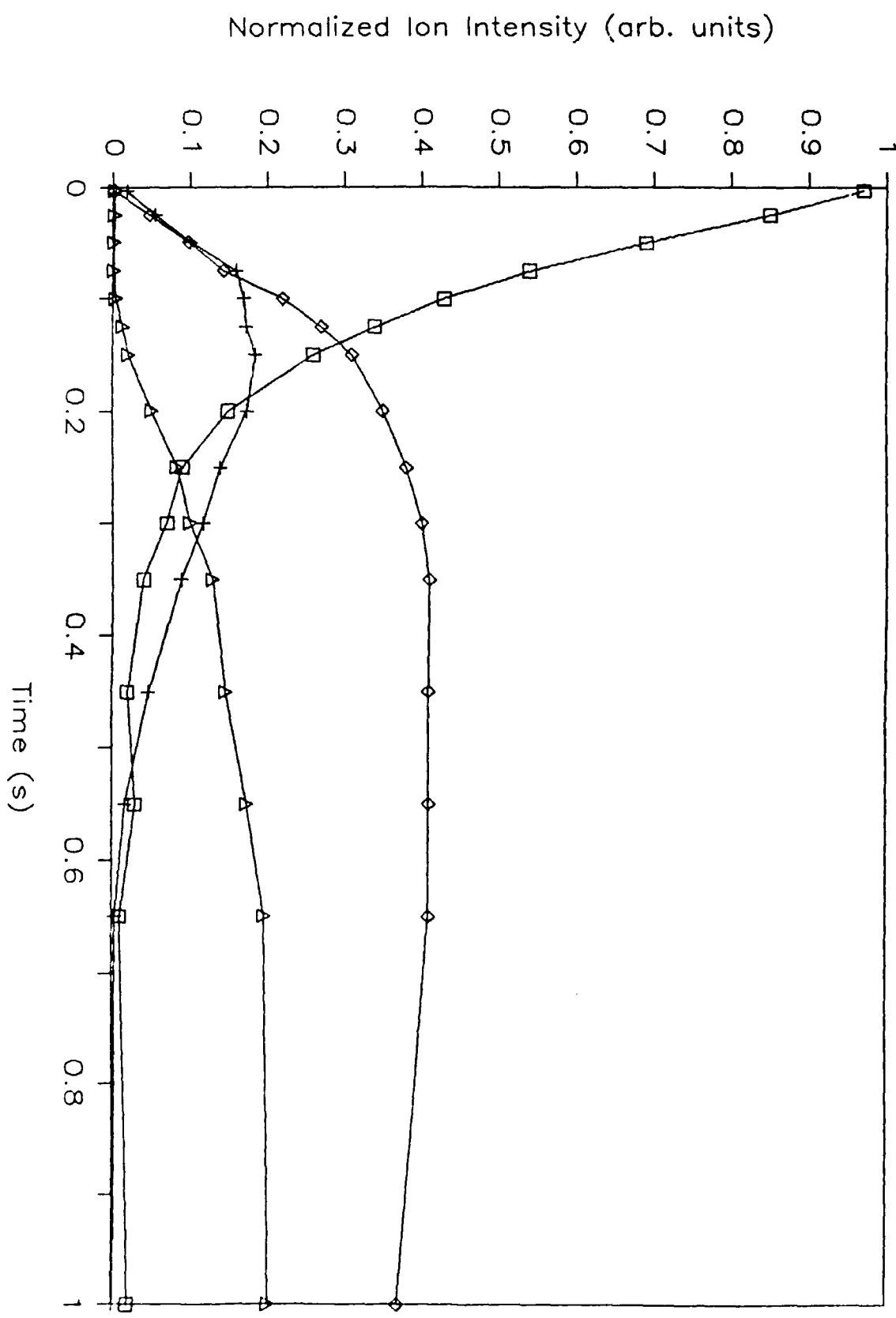


FIGURE 2a

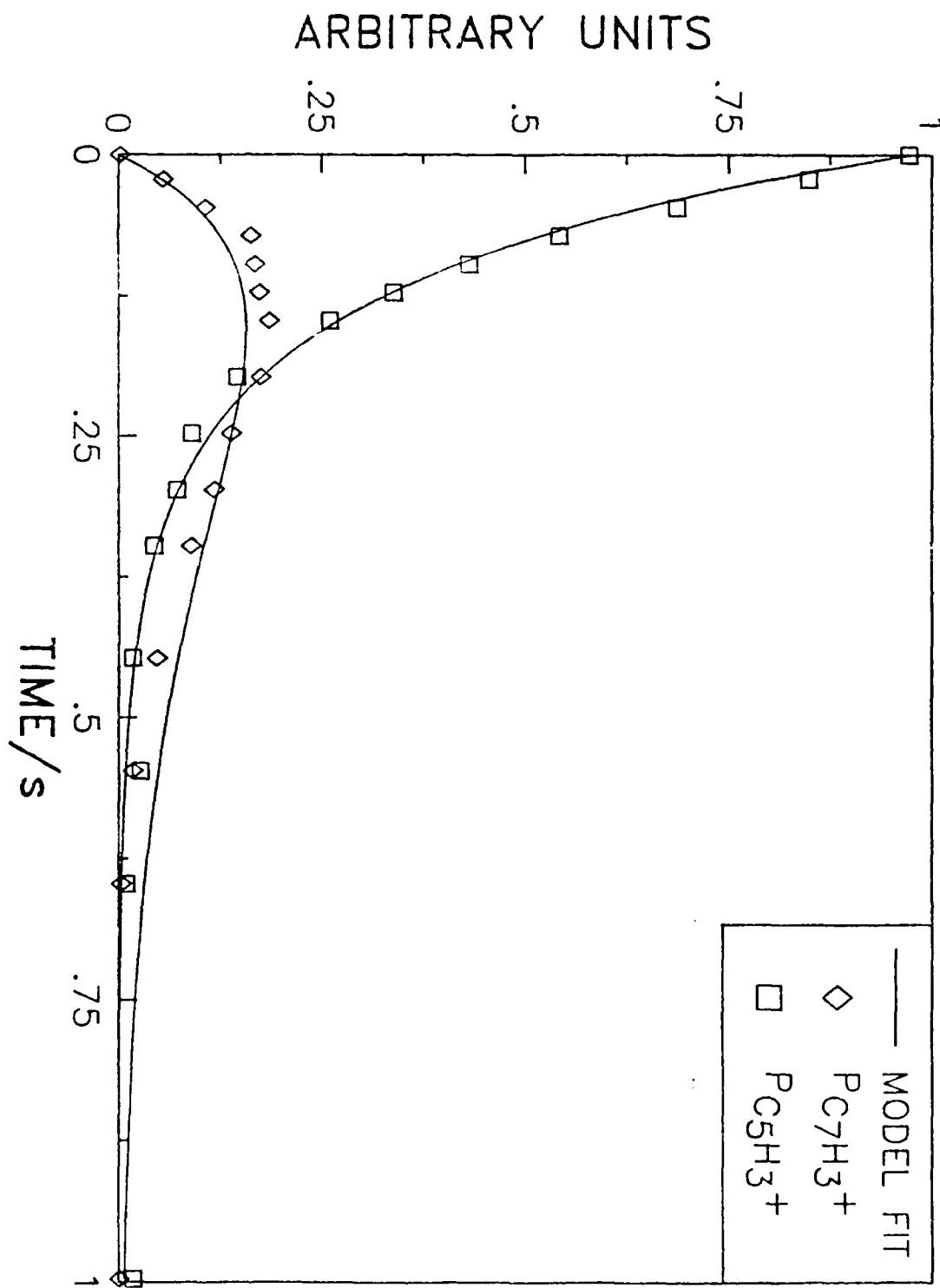


FIGURE 26

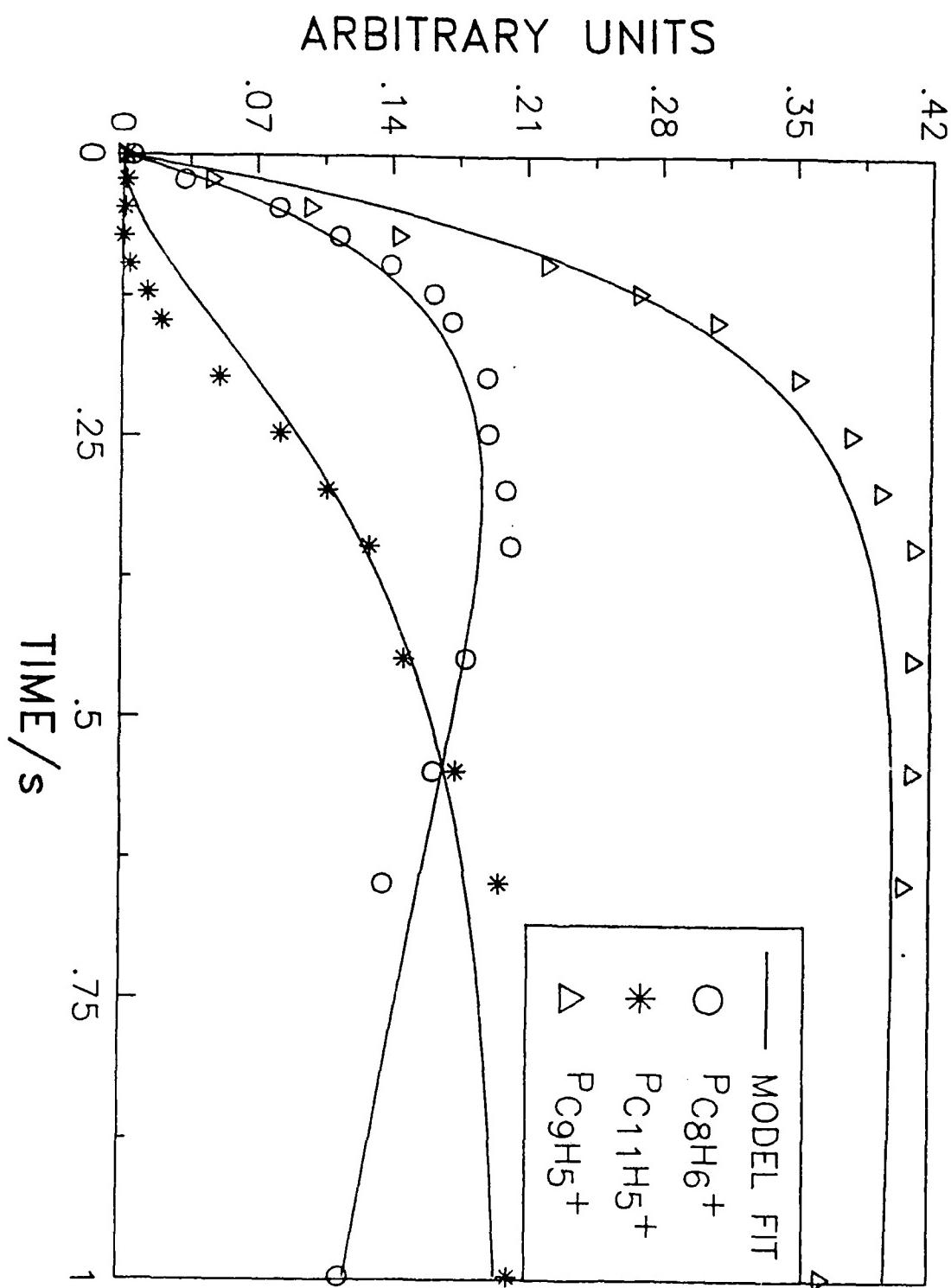


FIGURE 3a

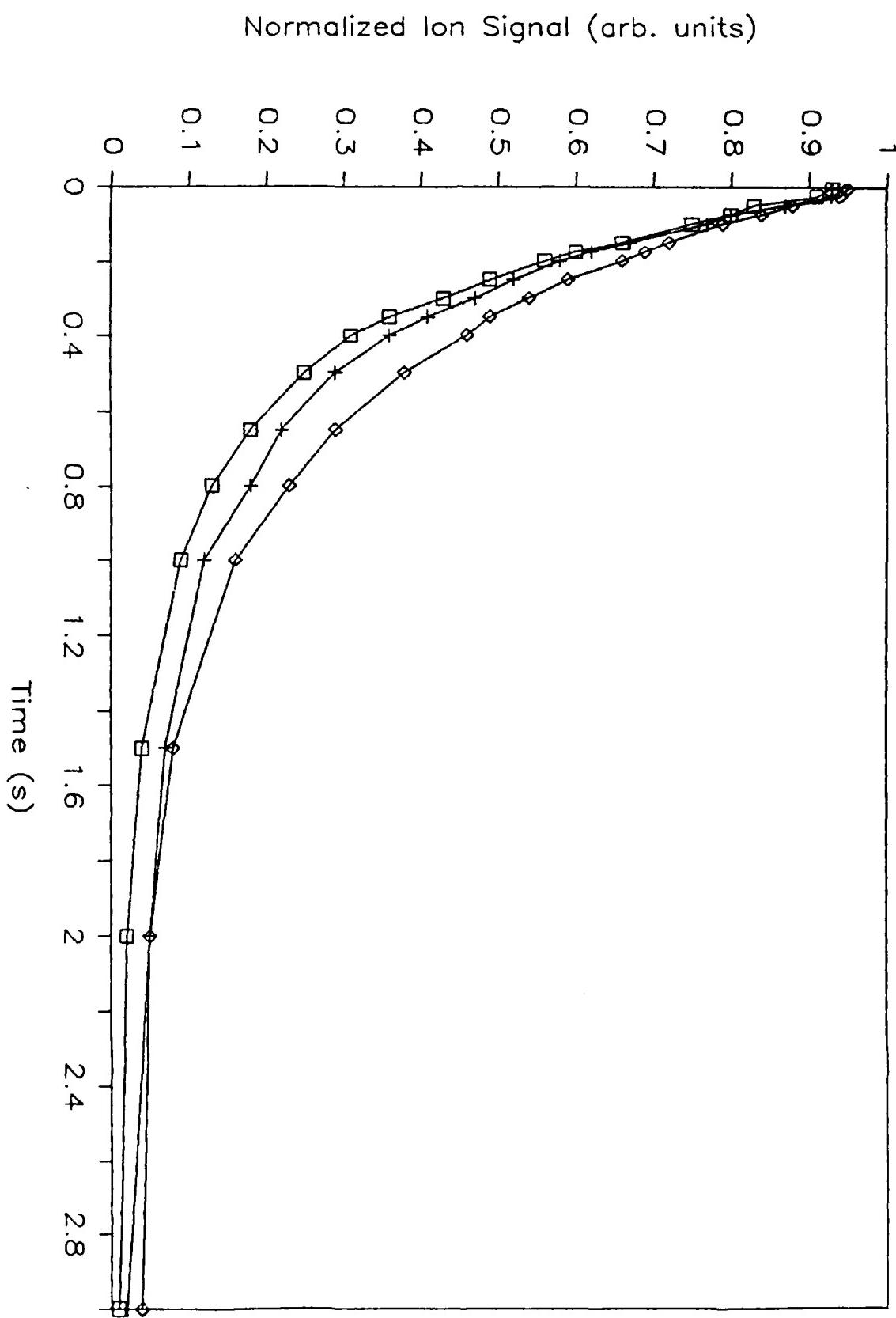


FIGURE 3b

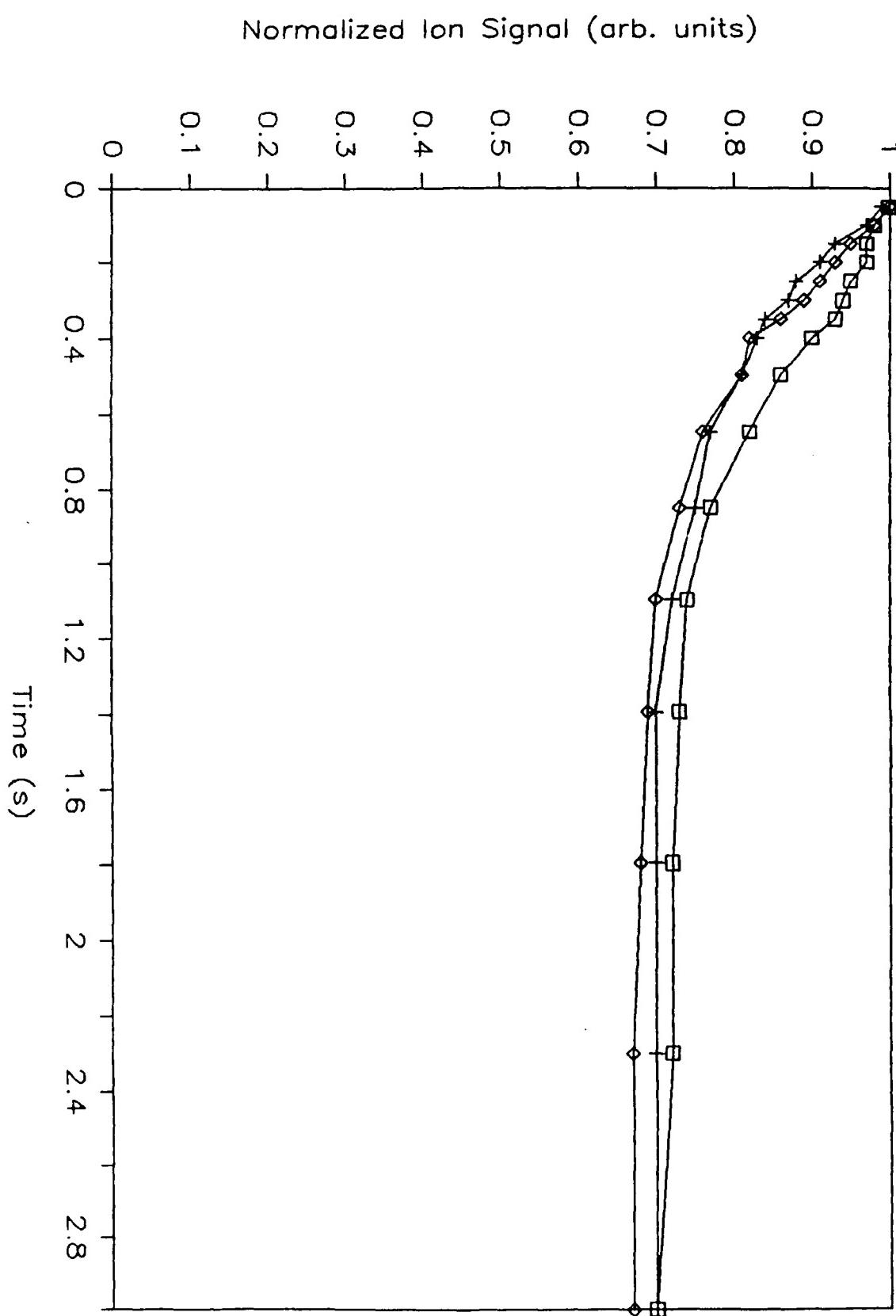


FIGURE 4a

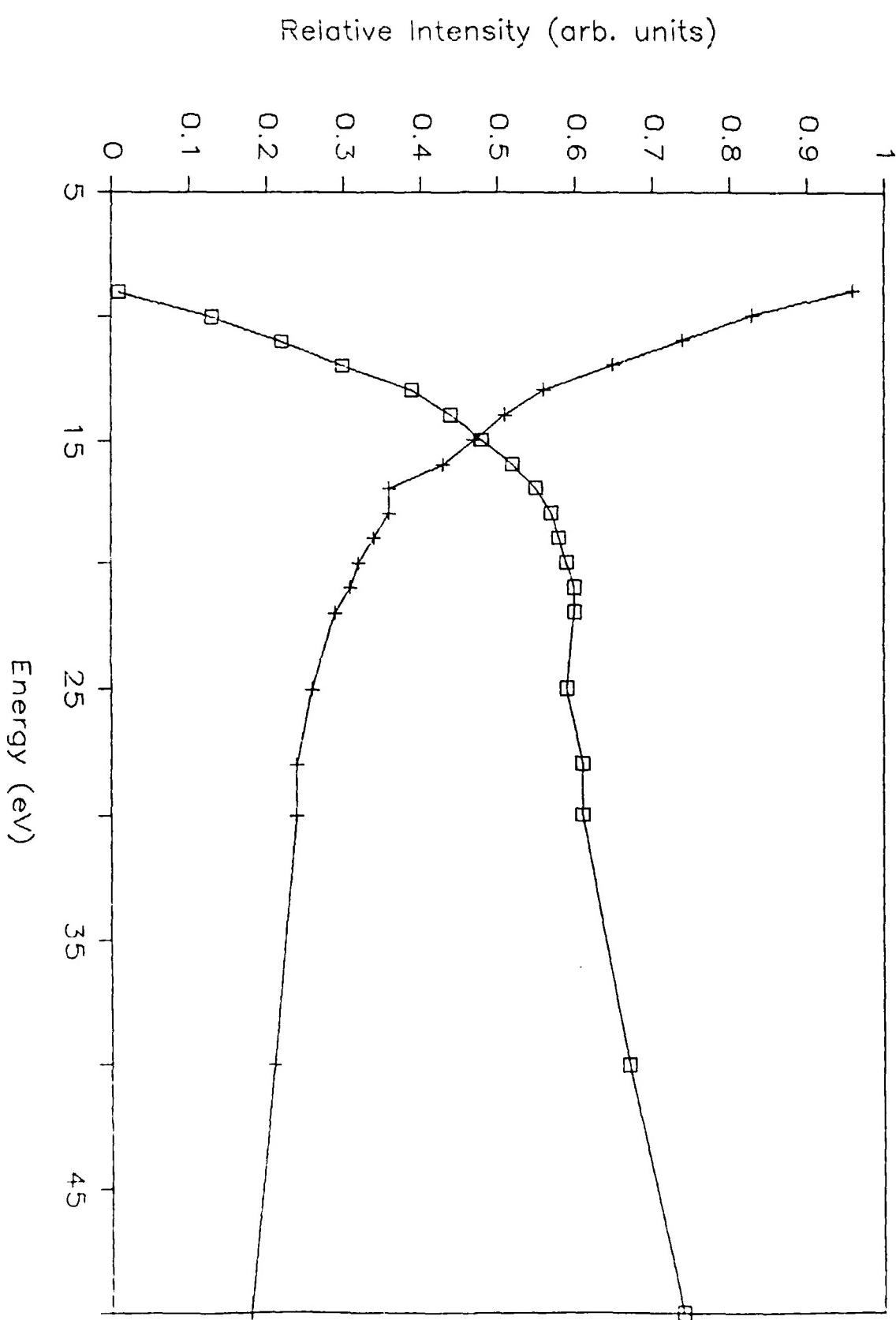


FIGURE 46

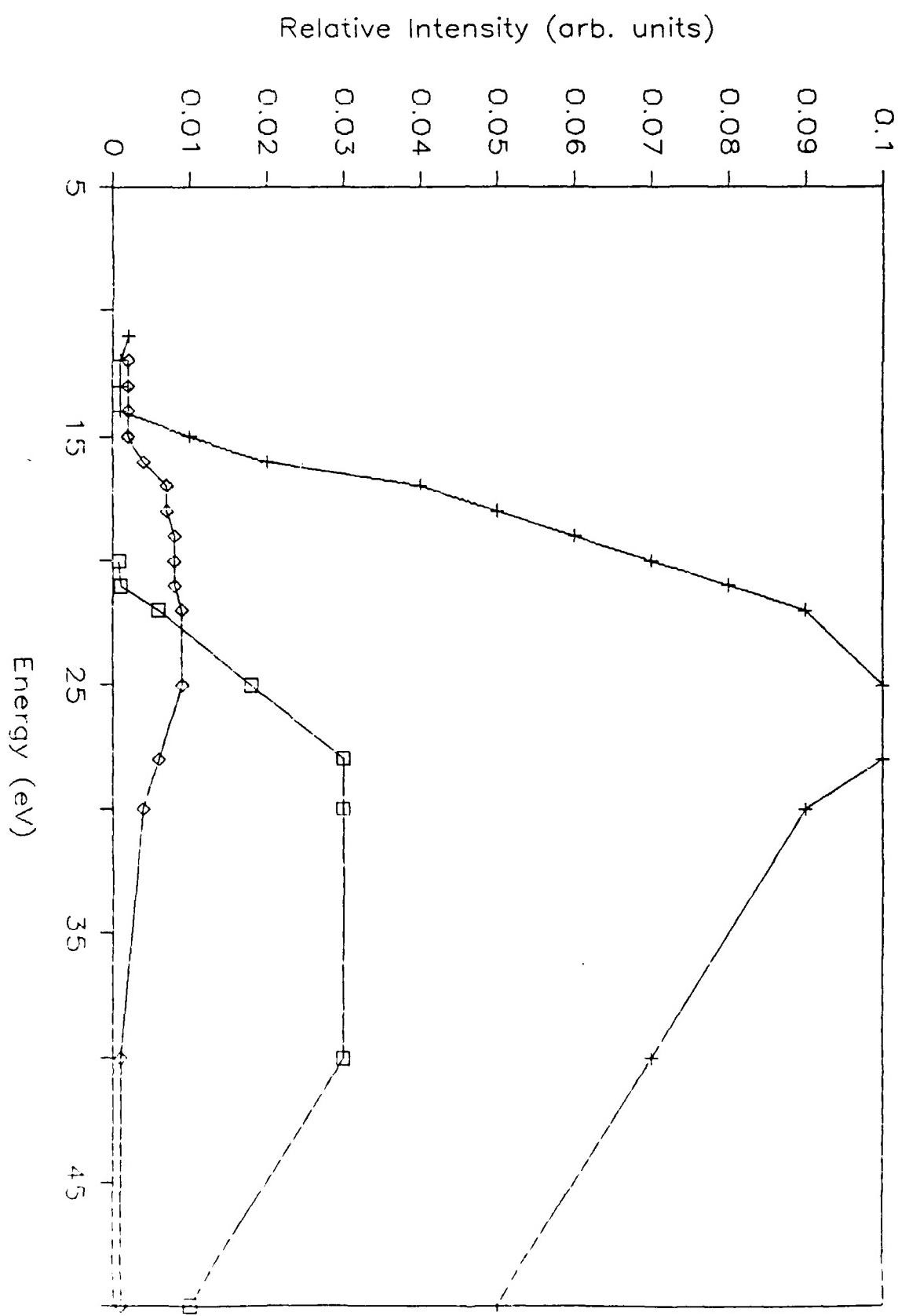


FIGURE 5a

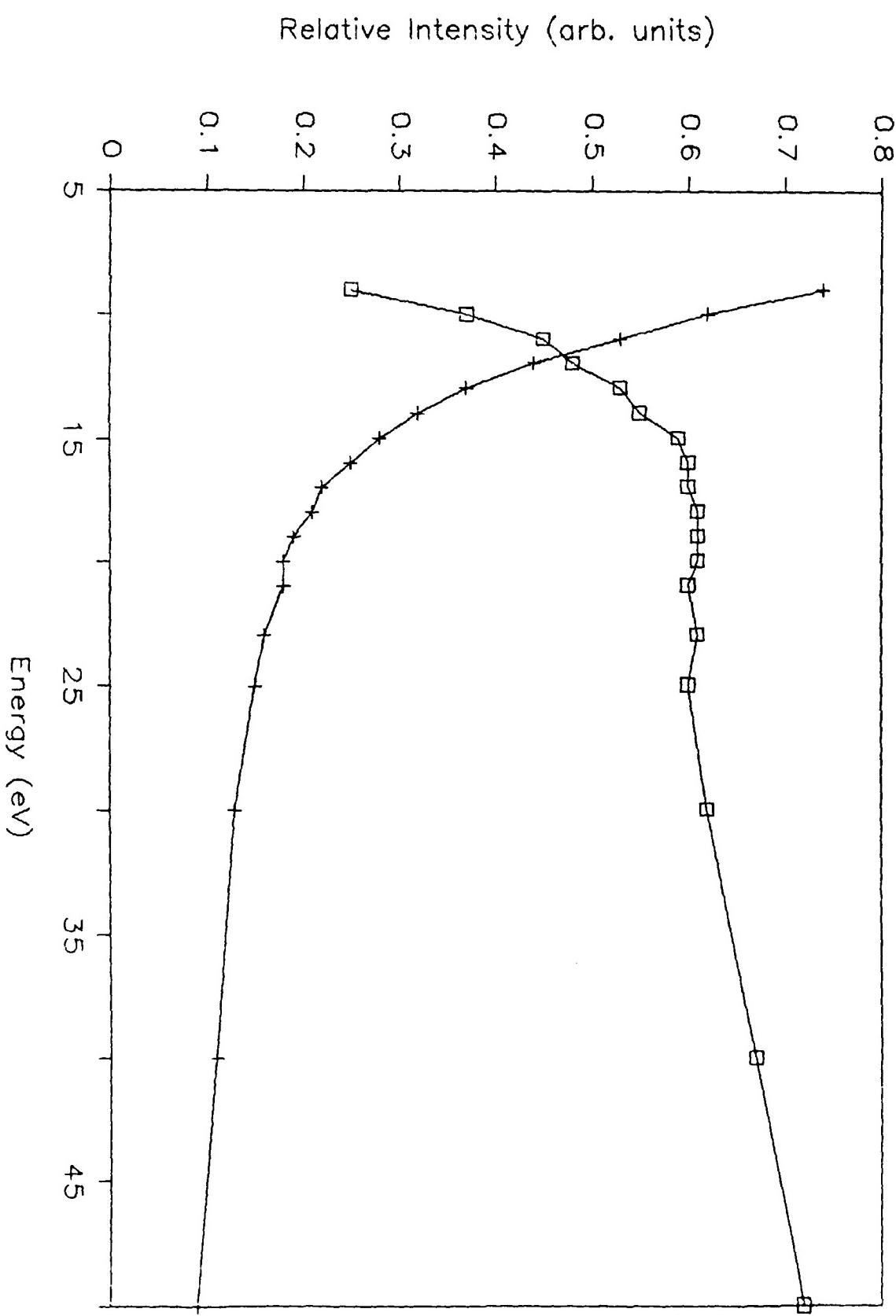
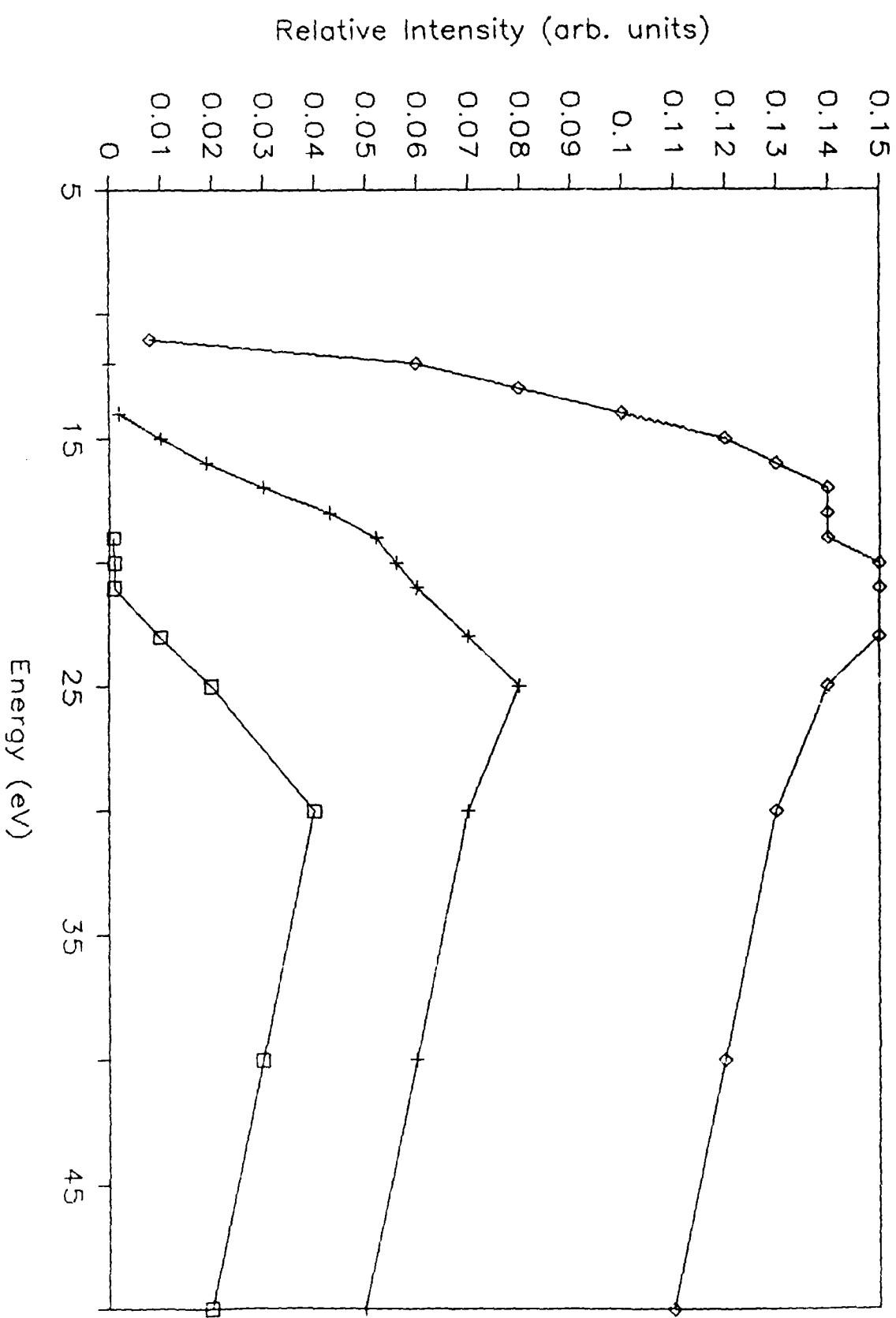


FIGURE 5b



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